

# **Current atmospheric monitoring of mercury in Japan and relating NIES activities**

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# Contents

- ◆ Long-term monitoring program for atmospheric mercury species and mercury in precipitation at background area (Cape Hedo, Japan)
- ◆ New site started at Oga, Akita prefecture
- ◆ Relating research project at NIES and NIMD collaboration

# Measurement items, sampling, and analytical methods

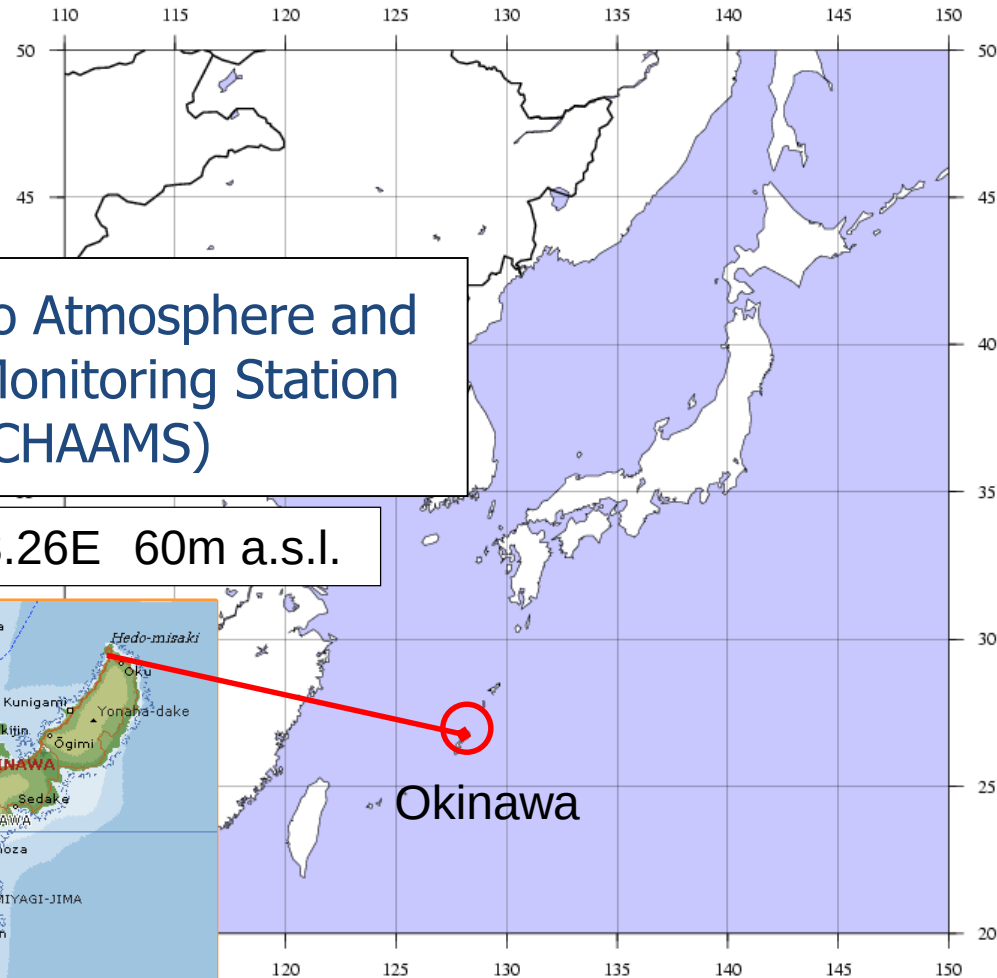
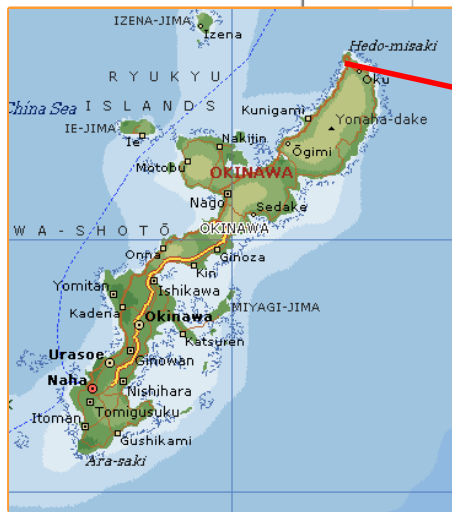
## Cape Hedo, 2007-current

| Component     | Measurement items  |                                                                                      | Sampling and analytical methods                                                    |
|---------------|--------------------|--------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|
| Atmosphere    | Mercury            | Mercury speciation (GEM, GOM, PBM)                                                   | Continuous measurement with Tekran mercury speciation system                       |
|               |                    | Hg                                                                                   | 24 hours continuous sampling by gold amalgamation method and followed by CVAAS     |
|               | Particulate matter | Pb, Cd, Cu, Zn, As, Cr, V, Ni, Se, Sb, Ba, Co, Mn, Sn, Te, Tl, Be, Al, Fe, Ca, Na, K | 7 days continuous sampling by the low-volume sampler and analyzed by ICP/MS        |
| Precipitation | Hg                 |                                                                                      | Sampling by the automatic wet-only sampler and analyzed by CVAAS (EPA method 1631) |

# Mercury monitoring station in Okinawa, Japan

Cape Hedo Atmosphere and  
Aerosol Monitoring Station  
(CHAAMS)

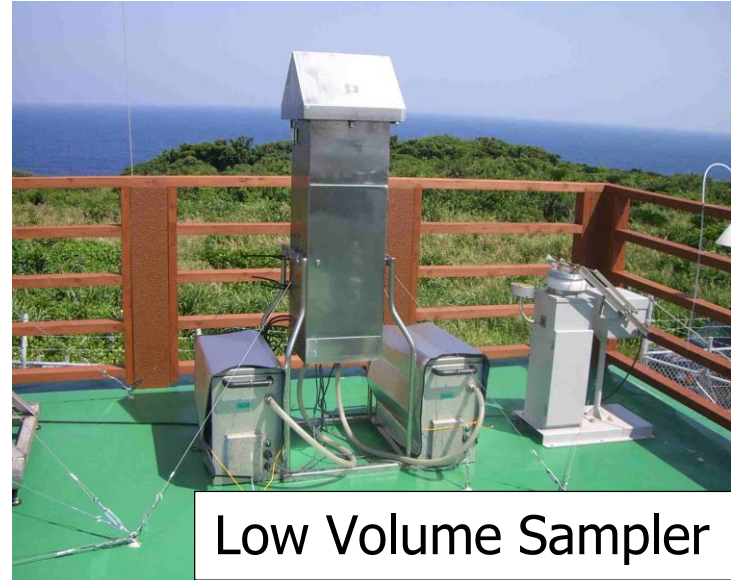
26.87N 128.26E 60m a.s.l.



# Sampling apparatus



Model 1130&1135  
Tekran Instruments



Low Volume Sampler



a glimpse of the monitoring site



Wet-Only Sampler

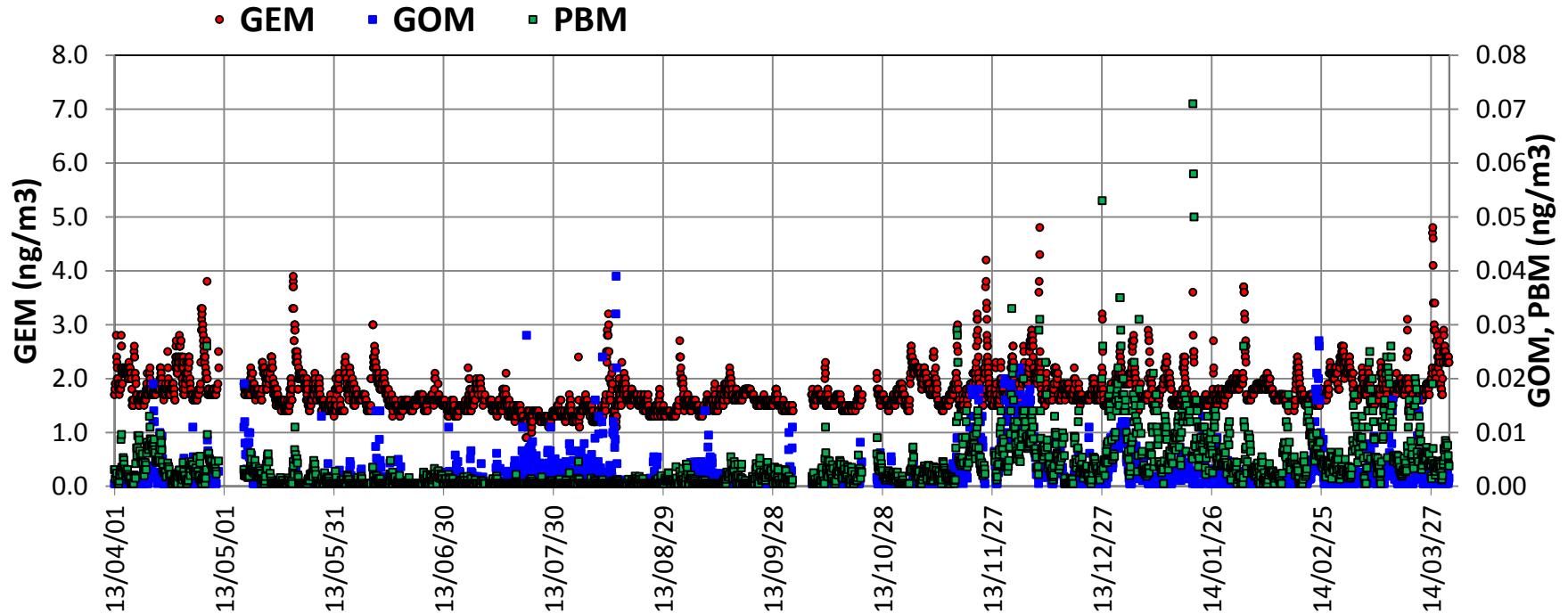
# Standard Operating Procedures for Atmospheric Mercury Analysis

## for Tekran mercury speciation system

- Develop the QA/QC procedure **in hot and humid conditions** based on Draft USEPA's SOP (Oct. 2008)
- GEM: Good correlation with MOEJ manual method\*
  - \* Measurement of gaseous mercury including GEM and GOM
- Good Recovery of manual injected STD Hg gas
- GOM, PBM: Good correlation with manually-operated offline method  
(Gaseous Elemental Mercury: GEM,  
Particle-Bound Mercury: PBM,  
Gaseous Oxidized Mercury: GOM)

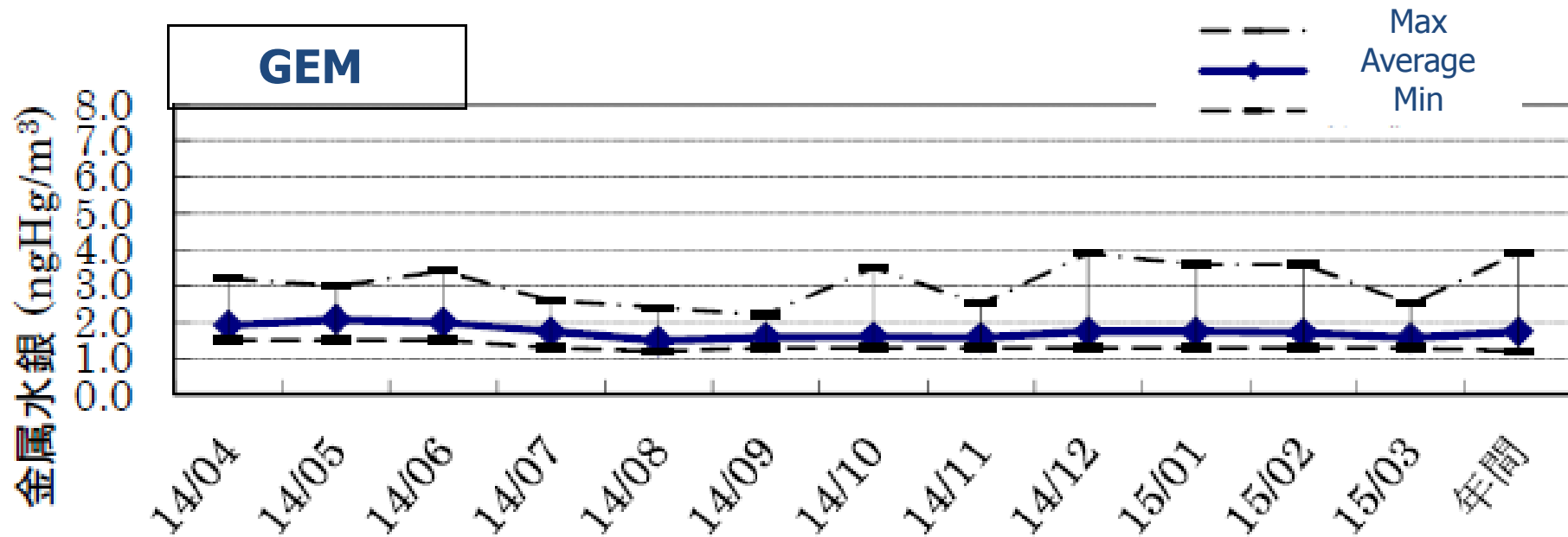
# Observations of mercury species

Cape Hedo, FY2014 (Apr 2014-Mar 2015)



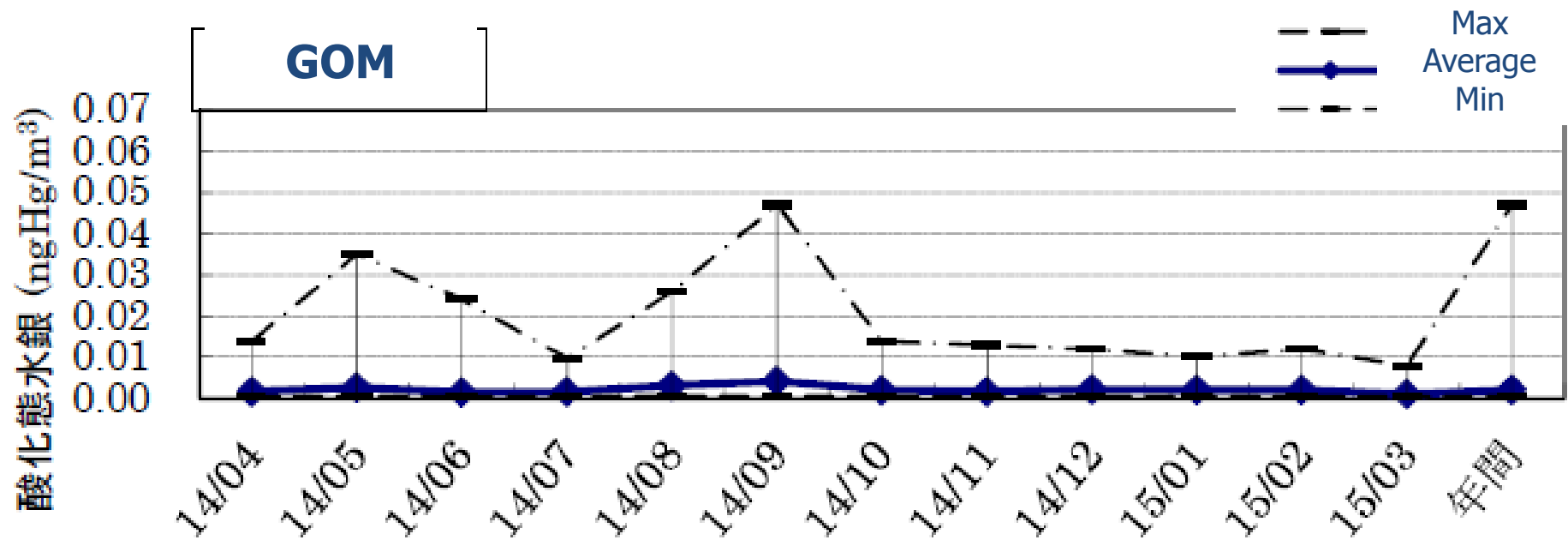
# Observations of mercury species

Cape Hedo, FY2014 (Apr 2014-Mar 2015)



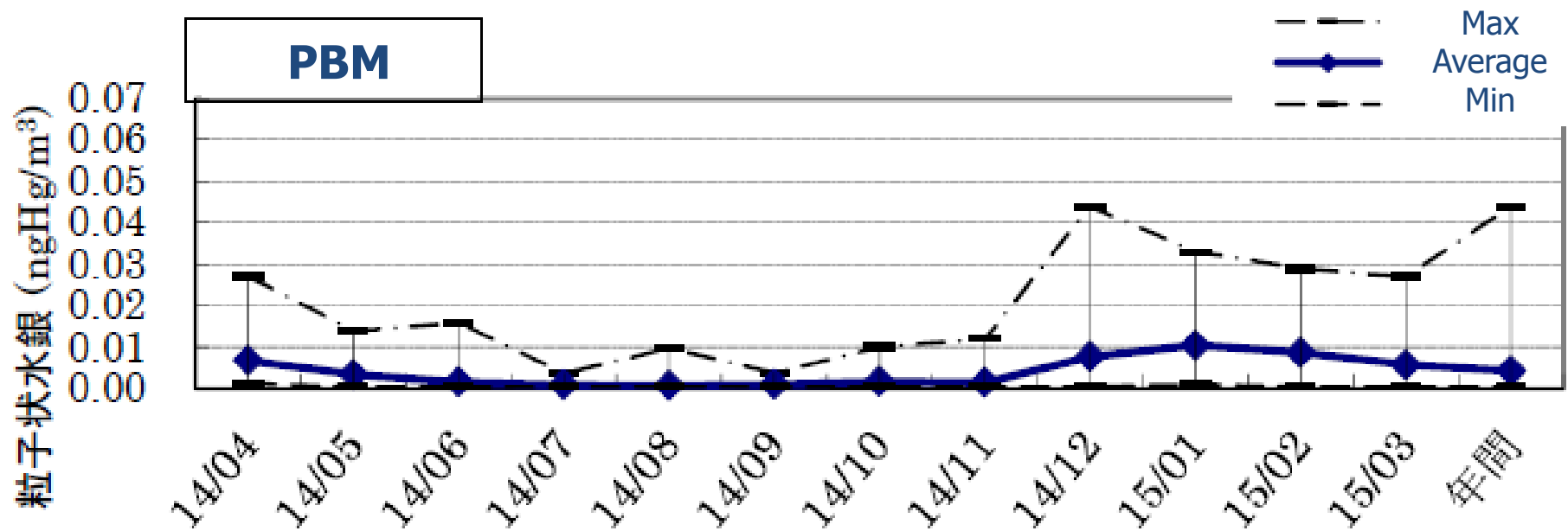
# Observations of mercury species

Cape Hedo, FY2014 (Apr 2014-Mar 2015)



# Observations of mercury species

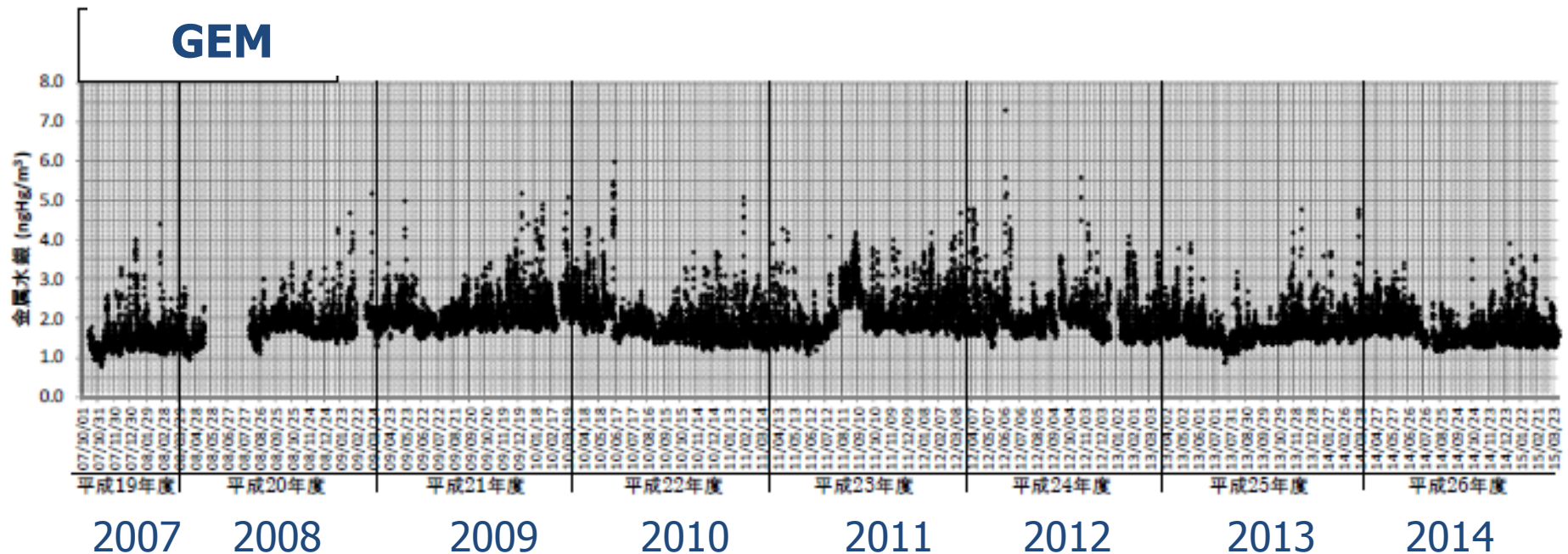
Cape Hedo, FY2014 (Apr 2014-Mar 2015)



# Observations of mercury species

Cape Hedo, FY2007-FY2014

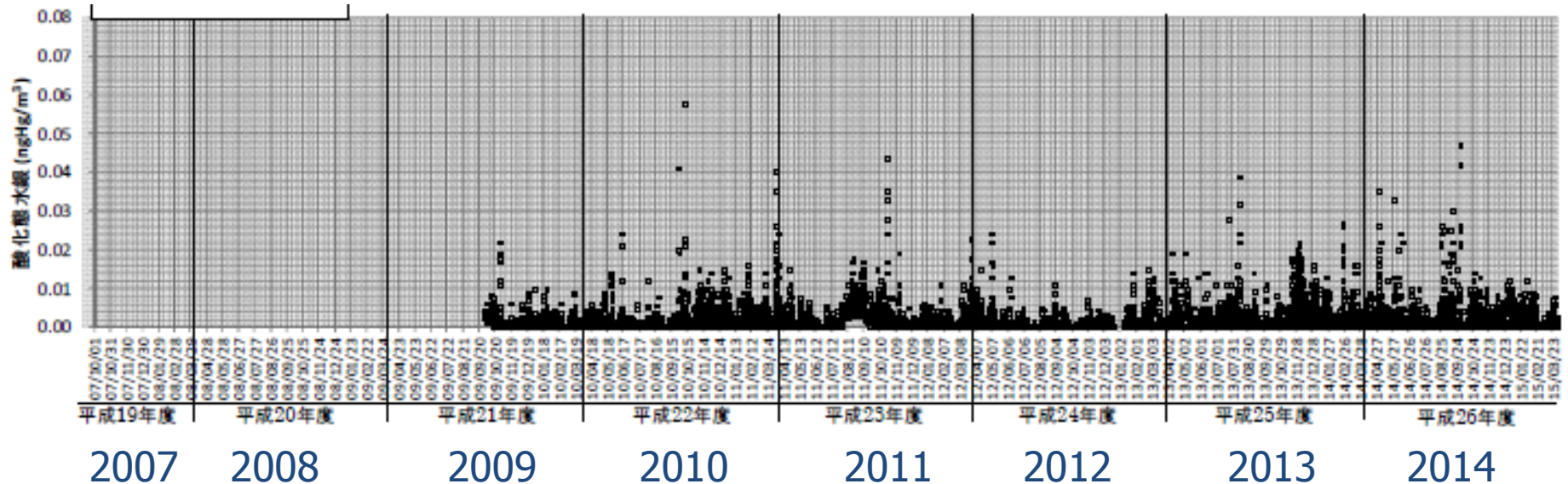
**GEM**



# Observations of mercury species

Cape Hedo, FY2007-FY2014

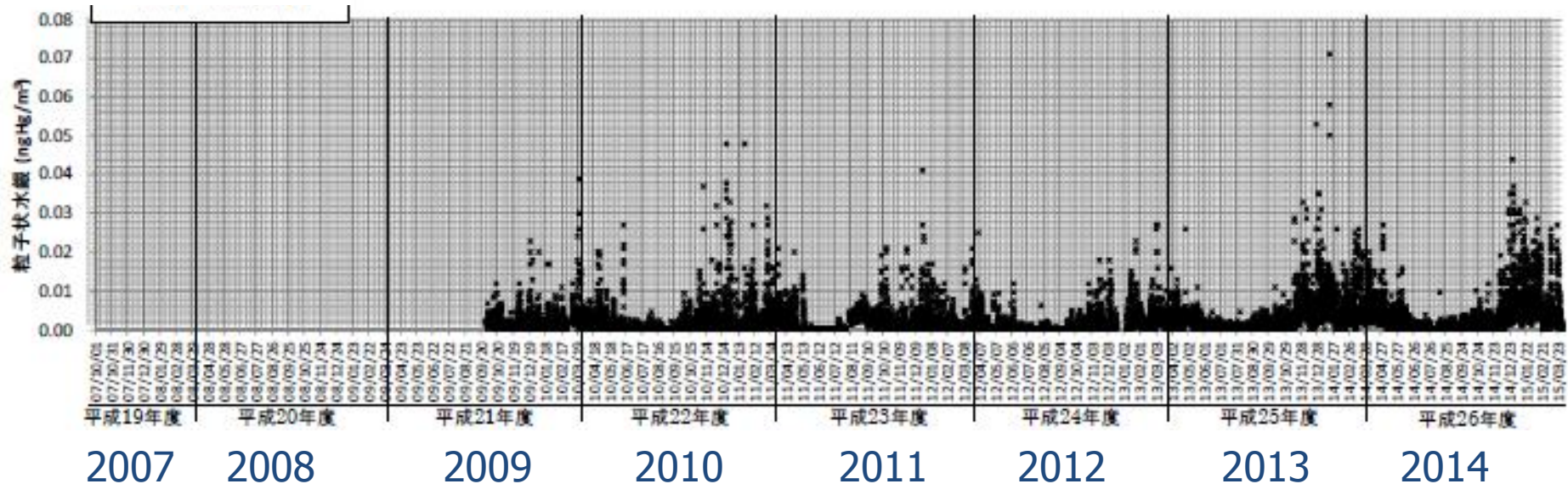
GOM



# Observations of mercury species

Cape Hedo, FY2007-FY2014

PBM



# Observations of mercury species

## Annual variations of GEM

### Statistics

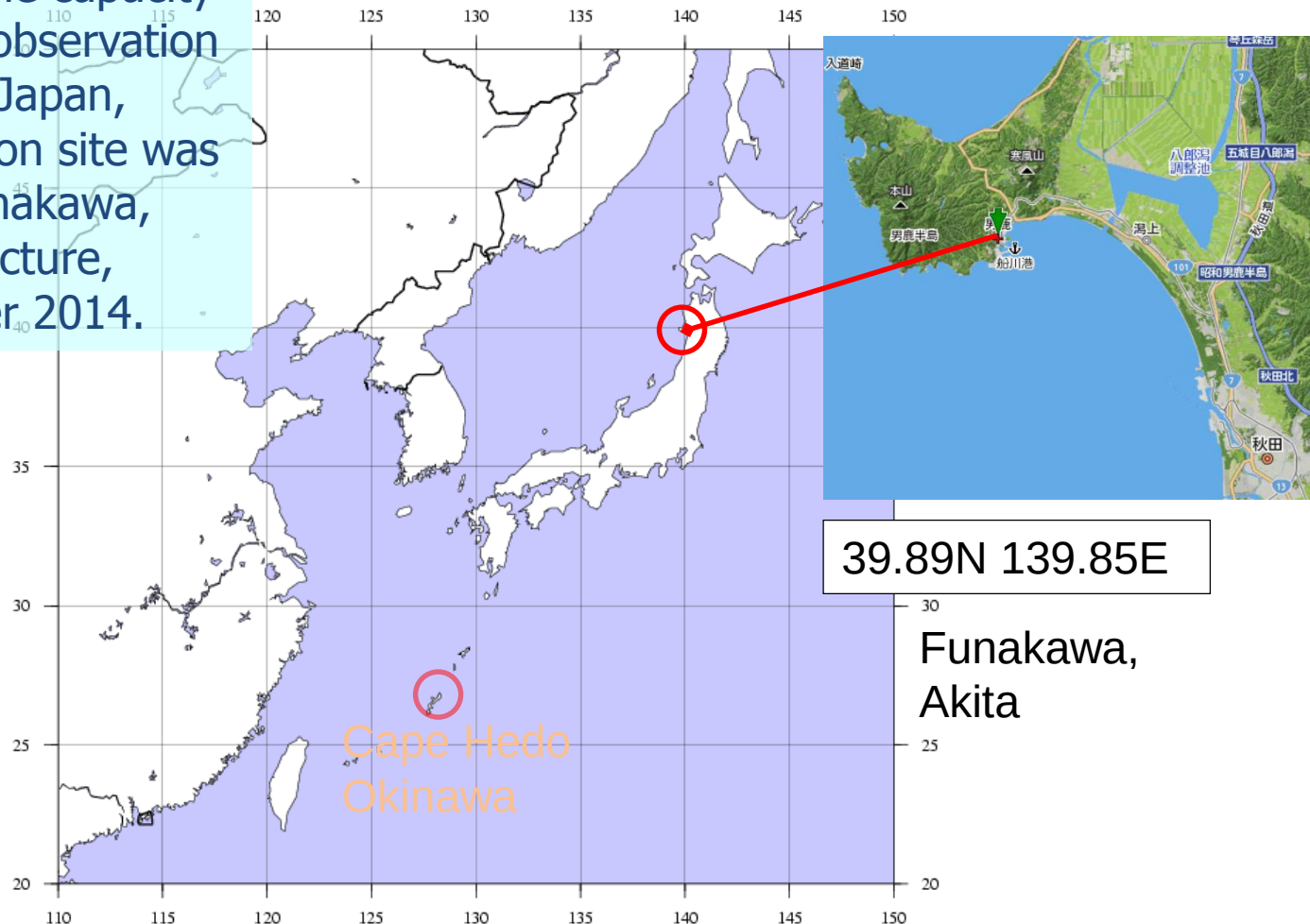
Hourly Mean of GEM

Unit: ngm<sup>-3</sup>

|                    | FY2008<br>(Apr 2008 - Mar 2009) | FY2009<br>(Apr 2009 - Mar 2010) | FY2010<br>(Apr 2010 - Mar 2011) | FY2011<br>(Apr 2011 - Mar 2012) | FY2012<br>(Apr 2012 - Mar 2013) | FY2013<br>(Apr 2013 - Mar 2014) | FY2014<br>(Apr 2014 - Mar 2015) |
|--------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| Mean               | 1.8                             | 2.2                             | 1.9                             | 2.1                             | 2.0                             | 1.7                             | 1.7                             |
| Median             |                                 |                                 | 1.8                             | 2.0                             | 1.9                             | 1.6                             | 1.7                             |
| Min                | 1.0                             | 1.5                             | 1.2                             | 1.1                             | 1.3                             | 0.9                             | 1.2                             |
| Max                | 5.2                             | 5.2                             | 6.0                             | 4.7                             | 7.3                             | 4.8                             | 3.9                             |
| Standard Deviation | 0.5                             | 0.5                             | 0.5                             | 0.5                             | 0.5                             | 0.3                             | 0.3                             |

# Mercury monitoring station in Akita , Japan

To strengthen the capacity of the mercury-observation network in Japan, a new observation site was set up at Funakawa, Akita Prefecture, in September 2014.



# Sampling apparatus

Model 1130&1135  
Tekran Instruments

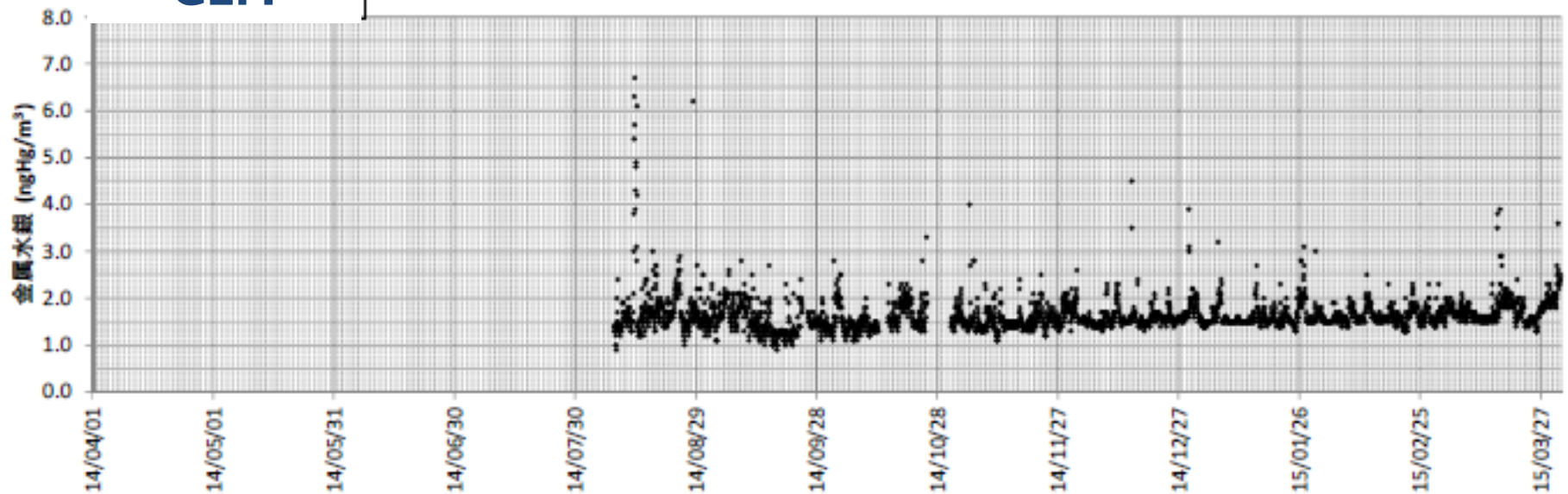


Wet-Only Sampler

# Observations of mercury species

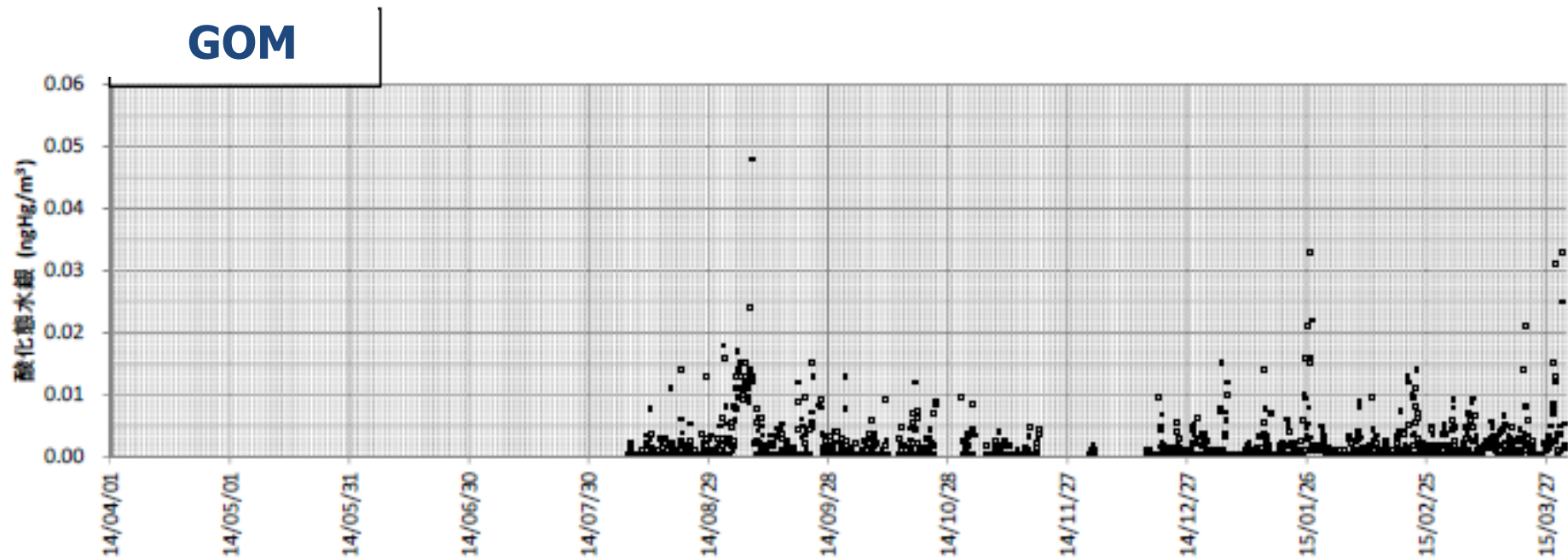
Cape Oga, FY2014

**GEM**



# Observations of mercury species

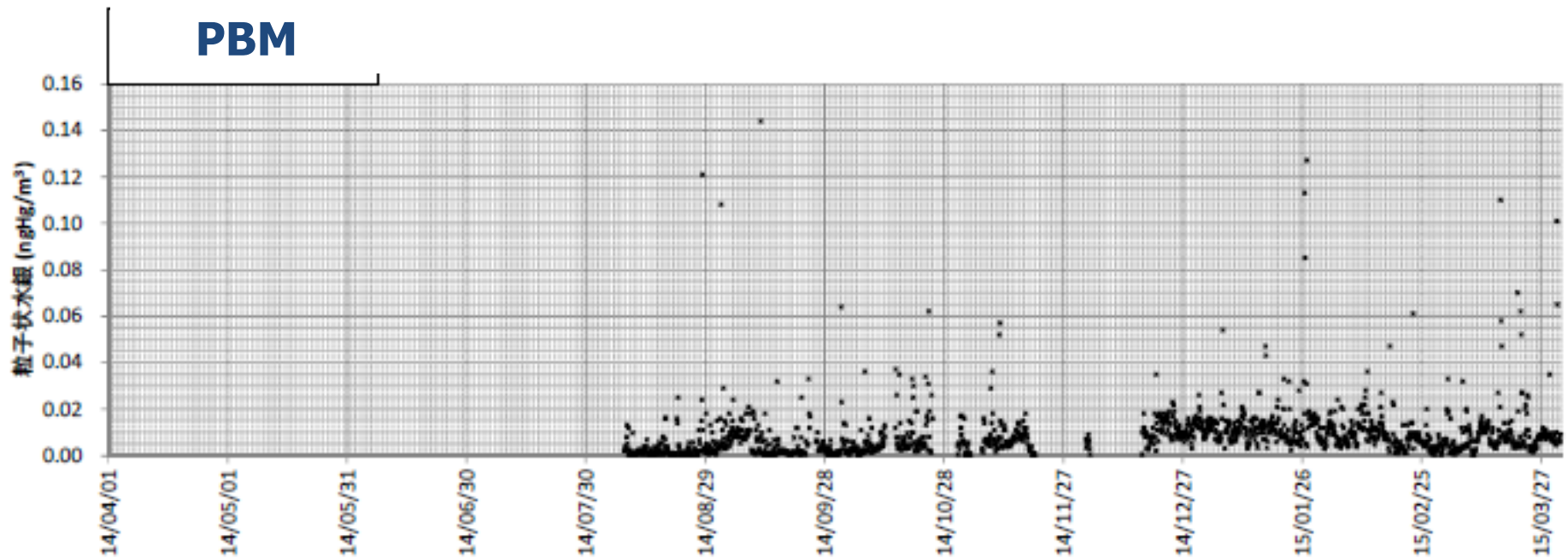
Cape Oga, FY2014



# Observations of mercury species

Cape Oga, FY2014

**PBM**



Observations of mercury species

# Annual variations of GEM

## At Oga site

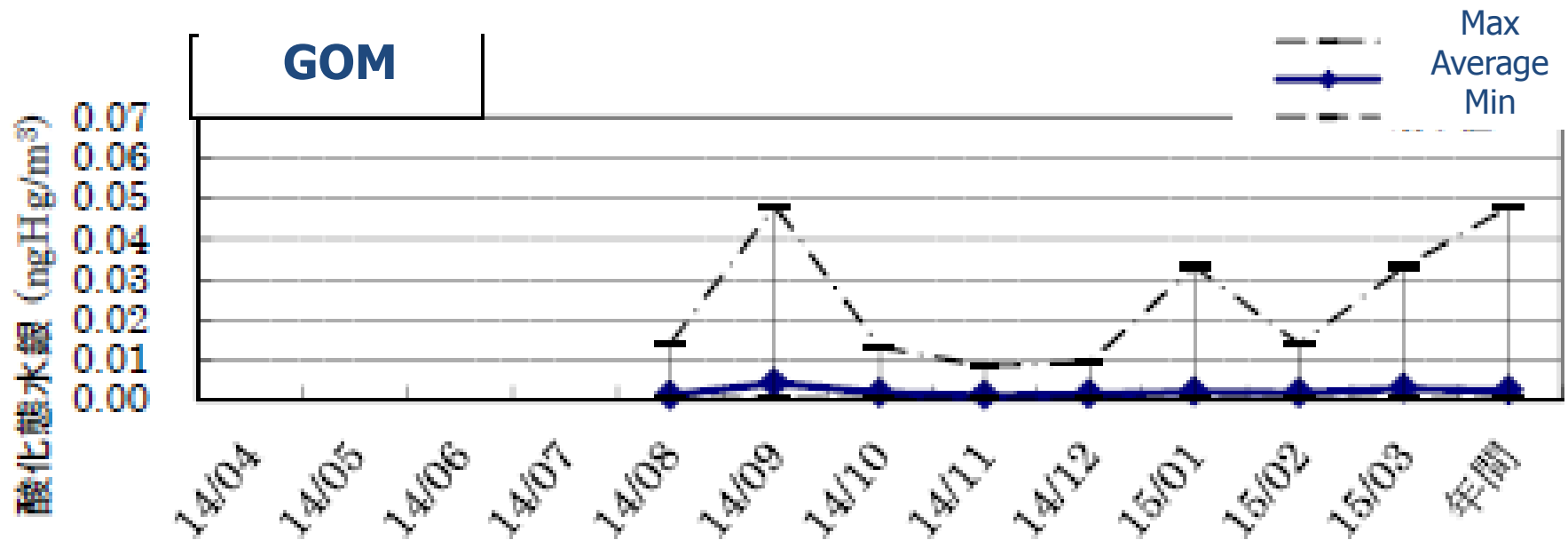
Statistics

Hourly Mean of GEM  
Unit:  $\text{ngm}^{-3}$

|                       | FY2014<br>(Apr 2014<br>- Mar 2015) |
|-----------------------|------------------------------------|
| Mean                  | 1.6                                |
| Median                | 1.6                                |
| Min                   | 0.9                                |
| Max                   | 6.8                                |
| Standard<br>Deviation | 0.4                                |

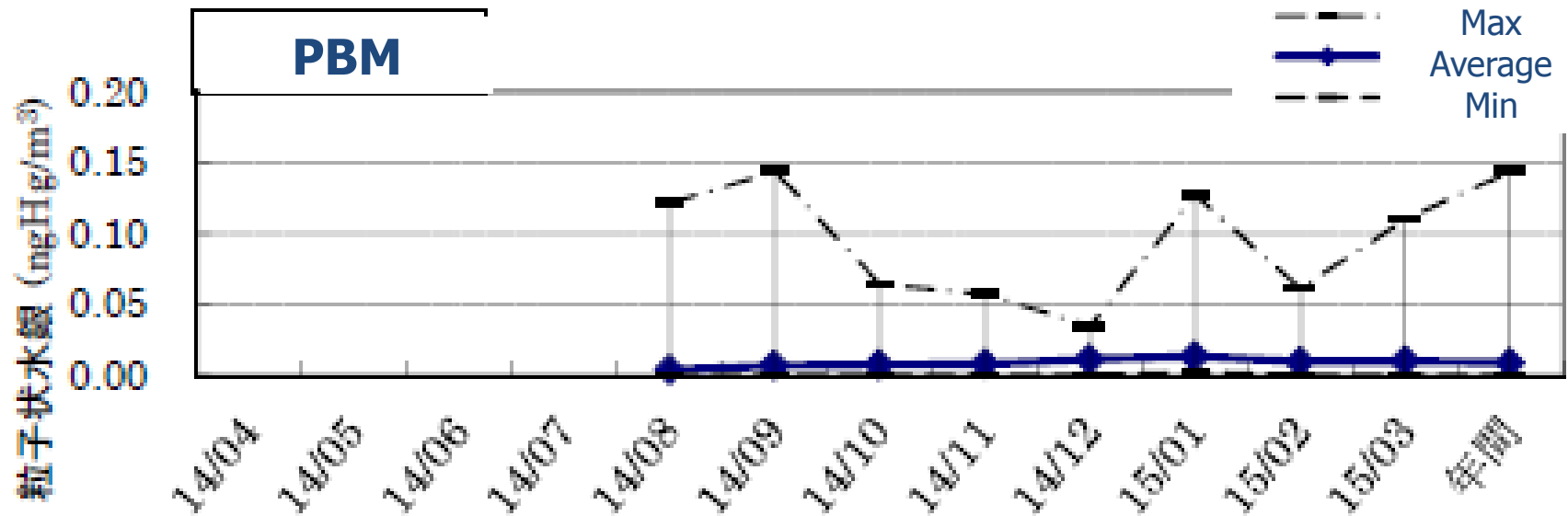
# Observations of mercury species

Cape Oga, FY2014 (Apr 2014-Mar 2015)

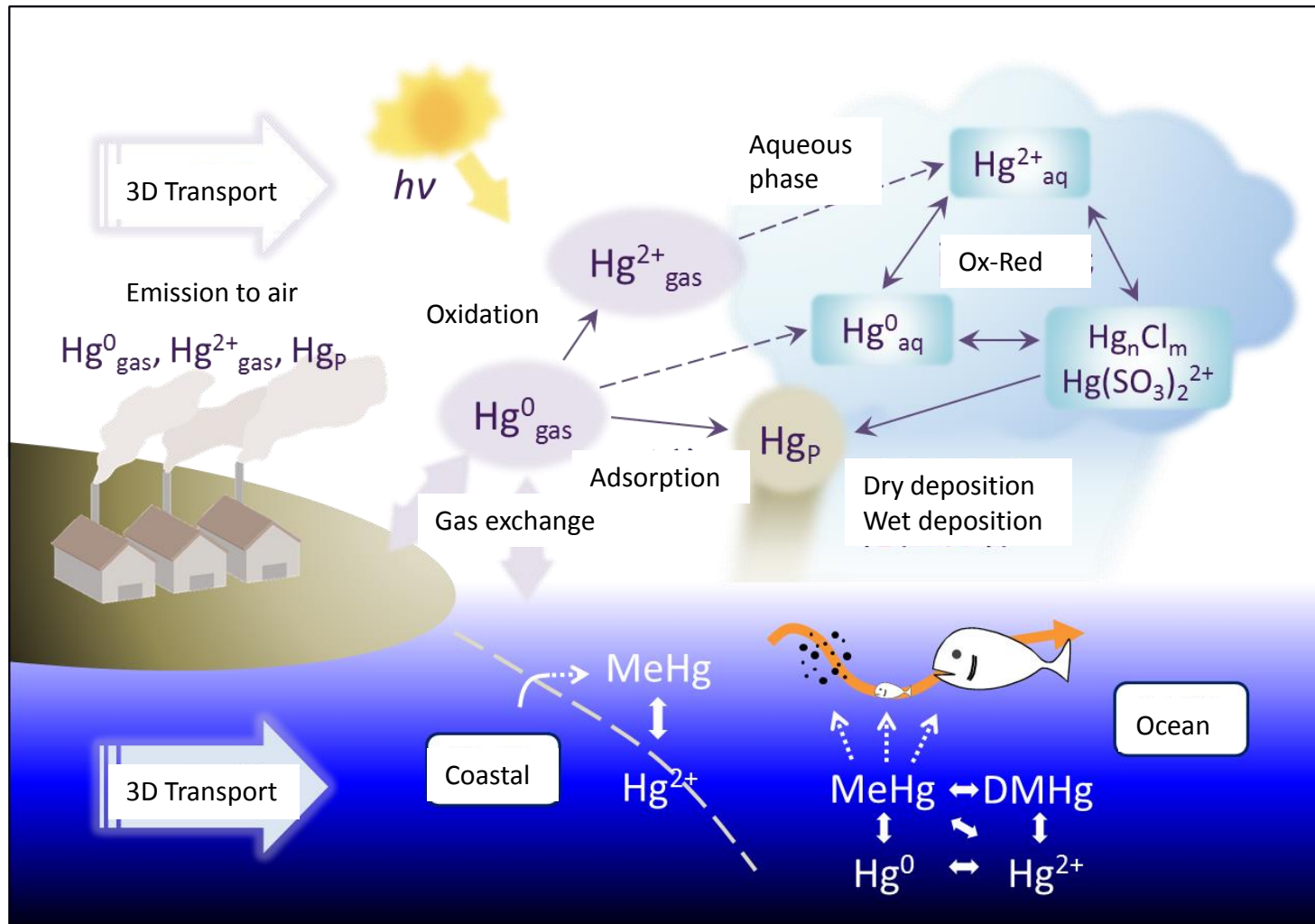


# Observations of mercury species

Cape Oga, FY2014 (Apr 2014-Mar 2015)



# Fate processes of mercury in global atmosphere-ocean system



# Analysis of mercury stable isotopes to reveal fate of mercury

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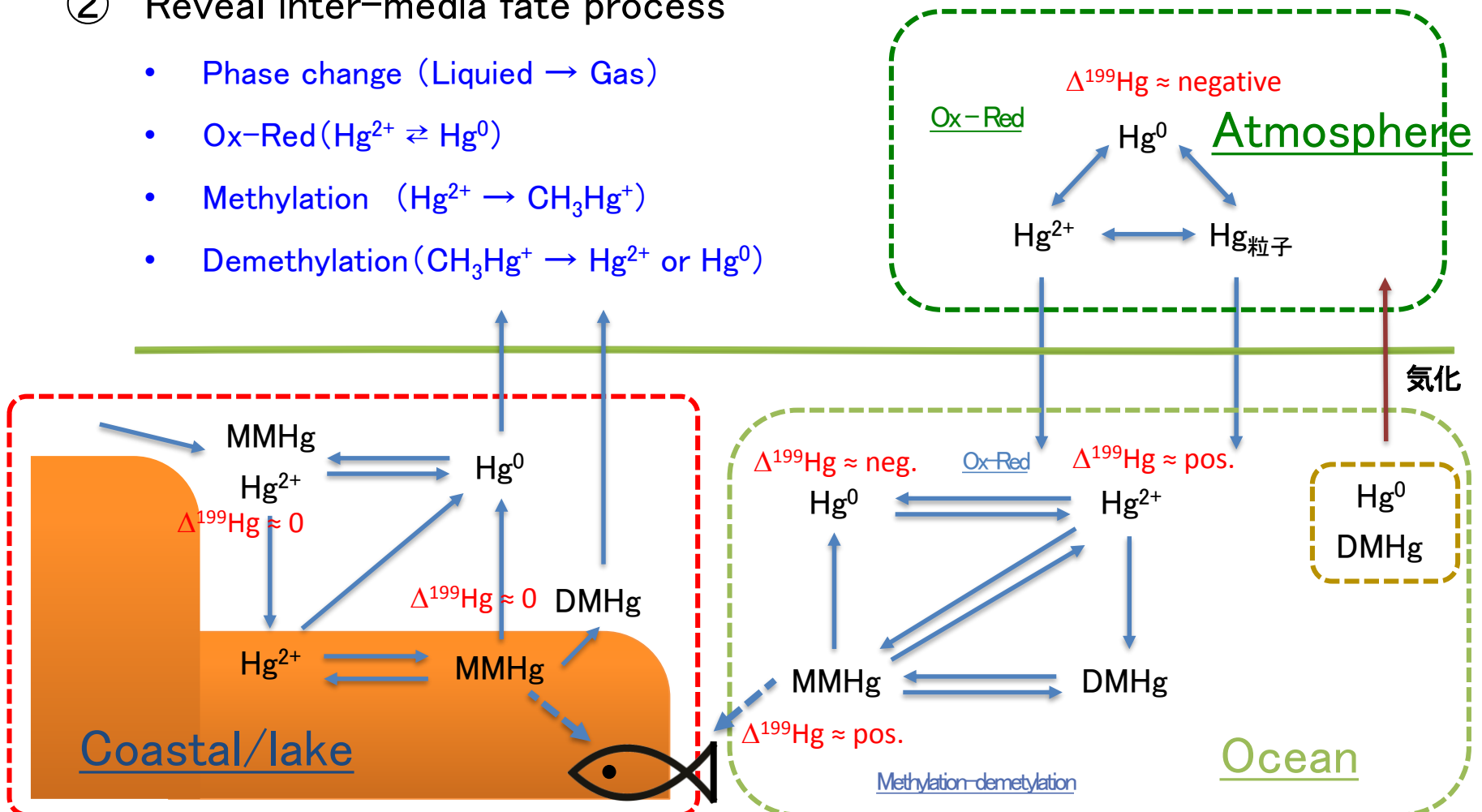
- General plan
    - Background and purpose
      - To analyze mass-dependent and mass-independent isotopic fractionation mainly in ocean-atmosphere system
      - Characteristic isotopic fractionation could imply specific chemical/physical process that the mercury species being suffered from ← volatilization, biological species transformation, etc.
      - ⇒ Expecting to reveal unknown location, medium and process of mercury fate in atmosphere-ocean system
    - MDF and MIF
      - To analyze MIF ( $\delta^{202}\text{Hg}$ , etc. ) and MDF ( $\Delta^{199}\text{Hg}$ ,  $\Delta^{201}\text{Hg}$ ) in remote and coastal fish and sediments and discuss the location/medium and processes
- $$\delta^{\text{xxx}}\text{Hg} = \{ [(\text{xxxHg}/^{198}\text{Hg})_{\text{sample}}] / [(\text{xxxHg}/^{198}\text{Hg})_{\text{std}}] - 1 \} \times 1000$$
- $$\text{xxx} = 199, 200, 201, 202$$
- $$\Delta^{199}\text{Hg} = \delta^{199}\text{Hg} - (0.252 \times \delta^{202}\text{Hg})$$

# Analysis of mercury stable isotopes to reveal fate of mercury

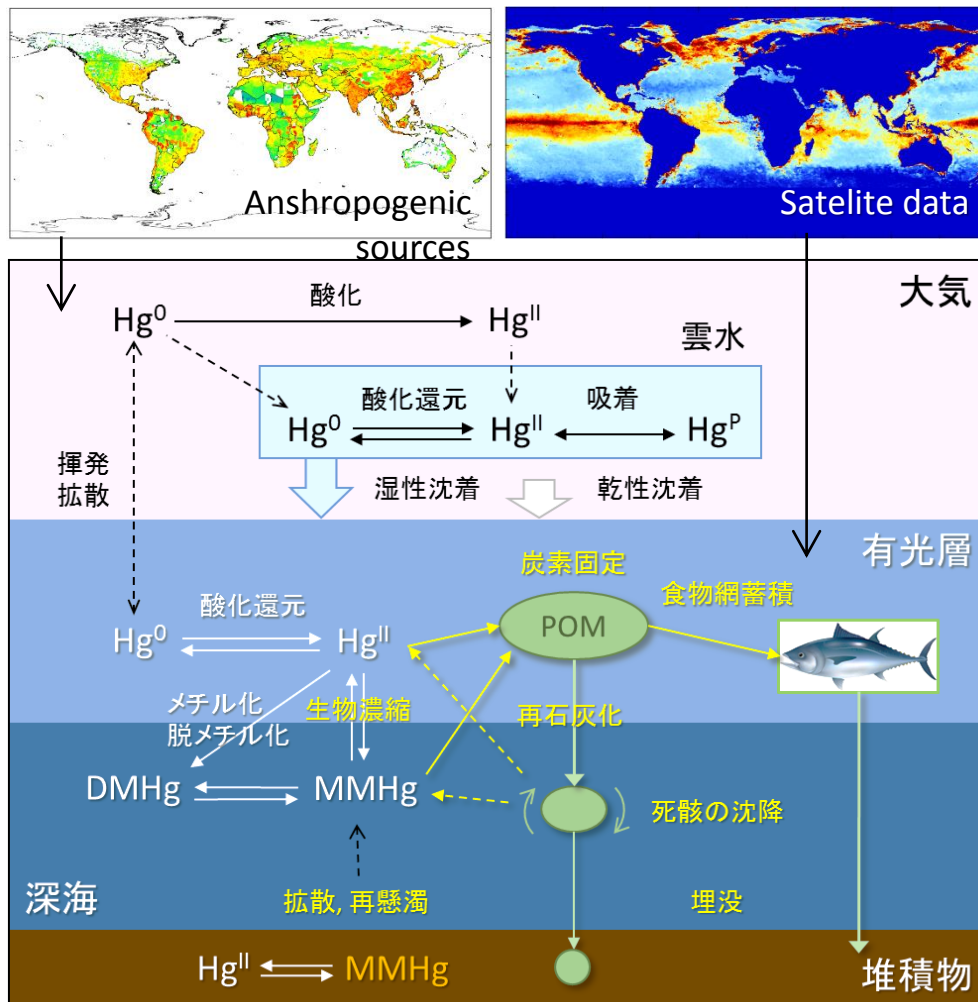
① Reveal sources of methyl mercury (Coastal or ocean or ?)

② Reveal inter-media fate process

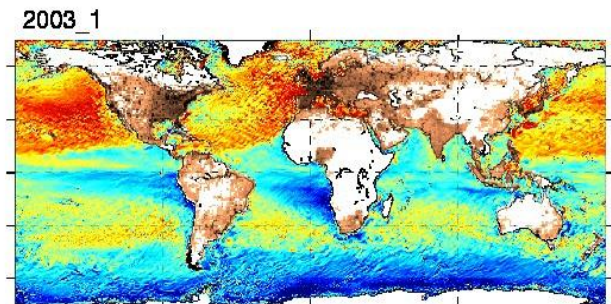
- Phase change (Liquid  $\rightarrow$  Gas)
- Ox-Red ( $\text{Hg}^{2+} \rightleftharpoons \text{Hg}^0$ )
- Methylation ( $\text{Hg}^{2+} \rightarrow \text{CH}_3\text{Hg}^+$ )
- Demethylation ( $\text{CH}_3\text{Hg}^+ \rightarrow \text{Hg}^{2+}$  or  $\text{Hg}^0$ )



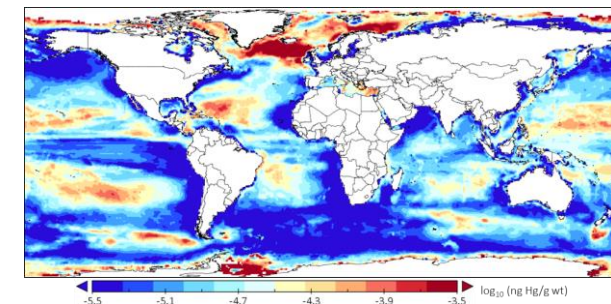
# Global multimedia fate model for mercury



Atmospheric long-range transport



Bioaccumulation in fish



- ◆ Atmospheric and oceanic transport, chemical reactions, bioaccumulation to be integrated
- ◆ Methylation process and location

# Summary

- **Continuous mercury measurement at Cape Hedo**
  - Starting in 2007, now continuous speciated monitoring by Tekran
  - Extensive QA/QC maintained based on established SOP
- **Trend of observation**
  - Around 1.8-2.0 ng/m<sup>3</sup> in average as GEM, maybe slight decreasing trend in recent a few years
  - New monitoring site Cape Oga opened this year, locating at northern part of Honshu island of Japan
  - Additional monitoring at Niigata prefecture
- **Relating activity**
  - Development of global multimedia fate model